THE RELATION OF PHYSICAL PROPERTIES TO STRUCTURE: A POWDER X-RAY DIFFRACTION INVESTIGATION OF INERT GAS HYDRATES

BY

RICHARD COLE

B.Ch.E., City College of New York, 1944
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

The purpose of this investigation was to obtain information about the structure of the so-called "inert gas hydrates" from powder x-ray diffraction patterns.

These hydrates are crystalline solids which may be characterized from several different standpoints. First, they are compounds of water and some other material which at room temperature is either a gas well above its boiling point or a volatile liquid. Second, the hydration number is always high, being never less than six and sometimes as high as seventeen. Third, the pure hydrates are stable only at low temperatures under ordinary pressures; a few are stable at room temperature under very high pressure of the hydrate-former.

Results

X-ray powder patterns of several hydrates of small gas molecules were obtained, and together with results obtained on a series of "small" hydrates by H. R. Müller[1] at the University of Bonn, they indicated that one structure for hydrate formation is a modified body-centered cubic lattice with a lattice constant of ca. 12A, space group O_h^3-Pm3n. A structure having a lattice constant of ca. 12A was then proposed by Dr. W. F. Claussen[2] of this laboratory to explain the x-ray and composition data for the "small" hydrates. The identical structure was subsequently and independently proposed by v. Stackelberg and Müller[3] and verified by them with the help of an intensity analysis. Pauling and Marsh[4] have also independently proposed the same structure and have verified it by means of an intensity analysis of their experimental results

for chlorine hydrate. There is reason to believe that Pauling was the first investigator to discover this structure.

Hydrates of larger molecules, such as the alkyl halides larger than methyl bromide, form another structure, having a modified face-centered cubic lattice (diamond type) with a lattice constant of ca. 17A, space group O_h^7-Fd3m. This structure was proposed by Claussen[5] and verified later by v. Stackelberg and Müller[1] with the help of an intensity analysis of powder x-ray data.

One general conception of the hydrate structure has been the packing of the hydrating molecules into void spaces in an ice-like lattice. In setting up his 17A structure (which was the first correct structure proposed for any of the gas hydrates), Claussen assumed that the basic void space was a pentagonal dodecahedron of water molecules. It is not surprising, therefore, that when the need for a 12A structure later became apparent, three different investigators discovered independently the same structure, which also had the pentagonal dodecahedron of water molecules as the basic void space.

The experimental work in this laboratory was confined to the 12A hydrates, which were formed in sealed thin-walled capillary tubes containing (a) water, and (b) liquid hydrate-former under its own vapor pressure, which in some cases was as high as 65 atm. at 25°C. The single hydrates studied were those of H_2S, CH_3Cl, CH_3Br, N_2O, CO_2, and Xe. The lattice constants varied from 12.01A for H_2S hydrate to 12.15A for CH_3Br hydrate. In general it was found that the larger the hydrating molecule, the larger the hydrate unit cell. A qualitative correlation of intensity distribution in the powder pattern with the size and scattering power of the hydrating molecule was also made. The critical decomposition temperature of each hydrate was measured by a direct melting-point method on the sealed tube used in the x-ray work. This measurement provided a check on the purity of the hydrates investigated. An attempt was made to prepare a compound

hydrate of CH_3Cl with H_2S, using different ratios of CH_3Cl to H_2S in the sealed capillaries, but x-ray and decomposition temperature measurements showed the products to be sometimes pure H_2S hydrate and sometimes a mixture of CH_3Cl hydrate and H_2S hydrate.

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VITA

The author was born on April 16, 1924 in New York City. He attended the public elementary and secondary schools of that city. After two years at Brooklyn College he transferred to The City College of New York, from which he received the degree of Bachelor of Chemical Engineering in 1944. Immediately after graduation he was inducted into the United States Naval Reserve and served in the American and Asiatic-Pacific Theaters.

Upon discharge from the Navy in 1946 he entered the Graduate College of the University of Illinois, from which he received the degree of Master of Science in 1948. During his graduate work he was a teaching assistant in physical chemistry for three years, and he also held research assistantships under contract with the United States Public Health Service and with the Office of Naval Research. During the academic year 1949-1950 he held a University Fellowship. He is the author of *Optimum Optical Density in Spectrophotometry,J. Opt. Soc. Am.* **51**, 38, (1951).

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